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Feature article

Mechanochemical remodeling of synthetic polymers

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ABSTRACT

In the past five years, the field of covalent polymer mechanochemistry has experienced a renaissance. Once limited to the simple scission of polymer chains, mechanical force can now be used to produce a wide array of productive chemistry. These outcomes have both challenged and supported classically held views of chemical reactivity. The impact of these findings has relevance in both synthetic chemistry and material science. Here, we review our efforts to exploit mechanochemical coupling to produce constructive and stress-responsive covalent chemistry in polymer materials.

1. Introduction

At the core of many applications of polymeric materials are their mechanical properties, and in particular their ability to withstand an applied load or stress. Mechanical forces are distributed (unequally) amongst the individual polymer molecules within a macroscopic material [1–4], and molecular responses dictate the material properties. For example, force-induced conformational changes along a polymer backbone might store the deformation energy, where it can eventually be released through entropically driven relaxation of an extended chain segment to a collapsed structure – the underlying basis of rubber elasticity [5–8]. Chemical or topological entanglements serve as anchors for the elastic response, pinning the ends of stress-bearing chain segments and preserving the stored energy [9,10]. Molecular responses, such as the scission of bonds or the slipping of chains through physical entanglement points, therefore regulate whether the deformation energy is stored or lost as viscous heat. These responses are accompanied by irreversible changes in structure at the molecular, mesoscopic, and macroscopic levels [11–13]. In a sense, one can think of the stress-bearing sub-chains as nanoscale devices for "force management", in that responses at the level of chemical bonds are ultimately tied to the macroscopic mechanical properties and to the failure or survival of the material under acute or chronic loading environments.

It should be considered in this context that there is a dramatic mismatch between the magnitude of the macroscopic and molecular forces that are typical of most applications: the mechanical forces that are typical of daily life (on the order of Newtons or greater) dwarf those between, for example, the atoms in a carbon–carbon bond (order $\sim 10^{-9}$ N). One consequence of this mismatch is that covalent bonds have been shown to break under certain macroscopic loading environments [14–16], and in some circumstances bond scission is believed to be an early stage of macroscopic material failure. Not only are macroscopic forces many orders of magnitude greater than atomic forces, they are also directional. They therefore differ from conventional forms of energy input such as heat and light, because specific nuclei can literally be pulled or pushed in a desired direction, for example along a particular reaction coordinate, overriding the reactivity preferences that are dictated by the electronic wave functions. In the past five years, several studies [17] have demonstrated that macroscopic mechanical forces can be harnessed at the molecular level, creating a new tool for the organic and materials chemist alike.

It has been noted that the opportunities in this area can broadly be divided into two categories [18]. First, there is the opportunity to develop new chemistry in the service of polymer science by designing and synthesizing mechanically active functional groups (mechanophores) and incorporating them into materials, in essence using chemistry to create new forms of "force management." This approach has the potential to elicit subsequent macroscopic responses, for example stress-sensing or stress-responsive properties. As we will discuss further over the course of this article, the fact that mechanical forces are often destructive ties into a specific

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vision along these lines, in which typically destructive forces are diverted into new *constructive* pathways that might enhance mechanical properties and prolong material lifetime. The second opportunity is the complement of the first – using polymers to transmit macroscopic forces to targeted molecules and drive chemical reactions that are either difficult or impossible to access by traditional methods. In relaying these concepts, we will focus on recent activity in our group, but draw on the many important contributions by others in context; a more general review has been recently published [17]. As is hopefully clear, both completed work and remaining challenges range from the fundamental to the applied. Potential applications include, in the realm of chemistry, new stoichiometric reactions and methods of catalysis, as well as stress-strengthening and self-healing polymers in the realm of materials. In a more general sense, we hope to better understand and leverage fundamental elements of chemical reactivity in regimes where force alters kinetic and thermodynamic behavior.

1.1. Overview of contemporary mechanochemistry

While polymer mechanochemistry has been known for decades [8,13,19,20], until recently its purview has been largely limited to the homolytic scission [19,21] of main chain carbon–carbon bonds under high shear flow [22]. The earliest forays into more specific bond activation by mechanical force targeted the scission of weak bonds such as metal-ligand coordination bonds [23–25] and covalent peroxide and azo linkages [26,27]. In 2007, following some preliminary success in the Moore group [27,28], Hickenboth et al. published a landmark paper in which they demonstrated that mechanical force can be utilized to drive constructive and selective chemical reactions. Here, the benzocyclobutene (BCB) moiety was tethered via two ester linkages to poly(ethylene glycol) (PEG) chains and Woodward–Hoffman disallowed cycloreversions were observed when the direction of the applied force opposed the rotation required to follow the allowed pathway [29]. Further examples from the recent literature include the sonochemical and solid state colorimetric ring opening reaction of spiropyran to merocyanine [30–32], the sonochemical reconfiguration of atropisomers [33], and mechanical dissociation of metal complexes [23,24,34,35], most of which have been recently reviewed by Caruso et al. [17]. Mechanically induced retro-Diels-Alder reactions [36] and subsequent thermal remending [37], along with the "unclicking" of the 1,2,3-triazole group [38] have been shown, elaborating on the utility of retrocyclizations in mechanochemistry. Fernandez and coworkers have used force microscopy to quantify the mechanical acceleration of disulfide bond scission in polyproteins [39]. Furthermore, mechanical intervention has been observed to affect small molecule reaction kinetics such as electrocyclic ring openings and the bimolecular dissociation of disulfide bonds coupled to stiff-stilbene bearing macrocycles [40–42], providing evidence that mechanical activation may not be strictly limited to macromolecules but may also be used to understand small molecule reactivity and find potential applications in synthetic transformations.

Our own interest and activity dates back to 2006. While investigating the material properties of metallo-supramolecular gels based on a family of van Koten-type pincer complexes [43–45], we realized that these complexes acted as defining motifs in supramolecular polymers; they were the active "force management" agents that dictated mechanical properties (Fig. 1). This direct molecule-to-material relationship allowed for the use of the principles of physical organic chemistry to predict the behavior of supramolecular polymers and better understand the underlying mechanisms of their mechanical response [46]. The utility of this approach stemmed from the fact that the dynamic mechanical response of the polymers could be related back to the kinetics of ligand exchange in the isolated pincer complexes [47–50]. While many of the networks' dynamic mechanical properties could be related to the force-free kinetics of the pincer complexes, it was clear that under certain circumstances force could accelerate the dissociation in the macroscopic systems; the gels could be physically torn apart, for example, on time scales much shorter than the force-free ligand dissociation rate. We therefore wondered to what extent force would accelerate the reaction, and whether we might be able to quantitatively relate macroscopic signatures to the force-induced kinetics, as we had done successfully with the force-free dissociation kinetics.

Using single-molecule force spectroscopy (SMFS), we determined that force does indeed accelerate the reaction, and that the rate of dissociation as a function of force extrapolated back to force-free reaction rates that match those of the model systems. Through these results, we were able to surmise that the reaction under force (up to ~200 pN) could be viewed as a continuous perturbation of the force-free reaction mechanism [25]. Different ligands and

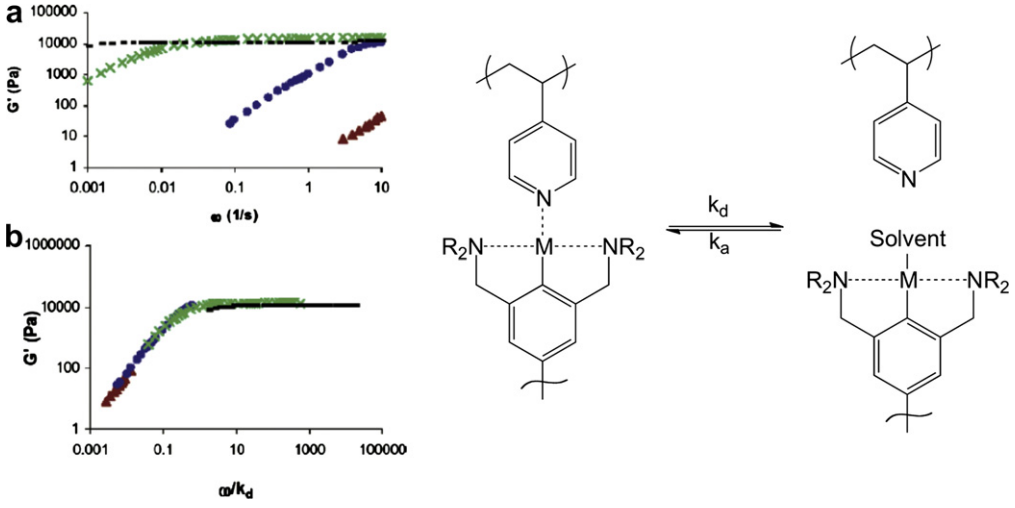

Fig. 1. Variations in storage modulus (G') are accounted for when normalized to the dissociation rates for a family of van Koten-type pincer ligands. Adapted with permission from Yount, W. C., Loveless, D. M., & Craig, S. L. Small molecule dynamics and mechanisms underlying the macroscopic mechanical properties of coordinatively cross-linked polymer networks. *Journal of the American Chemical Society, 127*(41), 14488–14496. Copyright (2005) American Chemical Society.

pincer complexes were compared, and the relative dissociation rates in the force-free reactions persisted in the force-accelerated reactions, establishing a connection between the action of an applied force and the reaction mechanism [25,51]. Knowledge of these relationships has proven useful in interpreting the non-linear viscoelasticity of supramolecular polymer networks [52–54], itself a form of structural polymer stress response, and we continue to use the pincer coordination chemistry as a mechanism by which to look for signatures of force-induced reactions in macroscopic polymeric materials.

The timing of the BCB work by Moore and coworkers was therefore quite propitious. Having been thinking about the fundamentals and consequences of force-induced reactivity in polymers, we were inspired by the force-induced BCB reactivity, not only because of its implications for new types of reactions, but even more so because it proffered a vision of using mechanical forces to form new bonds to polymers. This pioneering work gave a first voice to the idea that mechanochemical activation could be the basis of constructive covalent bond formation for stress-responsive polymers. We next outline the framework underlying our initial strategies in that area, and then review our accomplishments and failures to date. We end with a look ahead to the future of polymer mechanochemistry and the immediate challenges.

1.2. Mechanochemical remodeling as a platform for stress-responsive materials

Stress distributions in polymeric materials are typically heterogeneous [55], and regions of high stress concentration are generally regarded as the sites at which failure initiates [56]. The existence of these "at risk" regions create first an opportunity for material properties enhancement, but they also provide a critical challenge for the mechanophore strategy: the precise regions of high stress and failure initiation are difficult, and quite frequently impossible, to predict in advance. It is therefore desirable in many situations to disperse mechanophores at a high density throughout a polymer network. The thinking is that sufficiently high densities would ensure that a mechanophore is in the right place at the right time, without requiring *a priori* knowledge of stress distributions within a material. Relative to that of other activity in the field, our emphasis to date has therefore focused on the incorporation and consequences of multiple, non-scissile mechanophores in a single polymer chain. The ability to place many mechanophores on each polymer molecule, and to systematically vary that content, therefore provides one guiding principle of our initial design strategy.

Two additional design principles arise from our goal to understand the consequences of mechanically active functionalities that elicit constructive, and/or attenuate destructive, chemistry when exposed to a mechanical force. After high loading, the second design principle is motivated by the fundamental stress-strain behavior of single polymer molecules. Previous SMFS experiments [57–60] have confirmed the long appreciated theoretical picture of single polymer elasticity (Fig. 2), in which the compliance of the polymer is initially determined by entropic, conformational degrees of freedom. The force required to extend a polymer in this regime is quite low (0.1–50 pN). Once the conformational entropy is nearly exhausted, however, the force necessary to extend the polymer further increases rapidly, growing over a relatively small strain range from ~50 pN at the undistorted contour length to several nN of force, at which covalent bonds are broken [61]. Because forces on the order of hundreds of pN are necessary to have a dramatic influence on the rate of most covalent reactions, this means that mechanochemical activation without chain scission is only viable over a very narrow strain window in the extension of a polymer chain. To the extent that the goal is to prevent the bond-breaking events that initiate macroscopic failure, then, a second design principle is to trigger processes that increase the "active strain window" prior to chain scission through molecular "stress relief" -a force-induced increase in the covalent contour length of the polymer, allowing individual polymer chains to survive strains that would otherwise be catastrophic (Fig. 2).

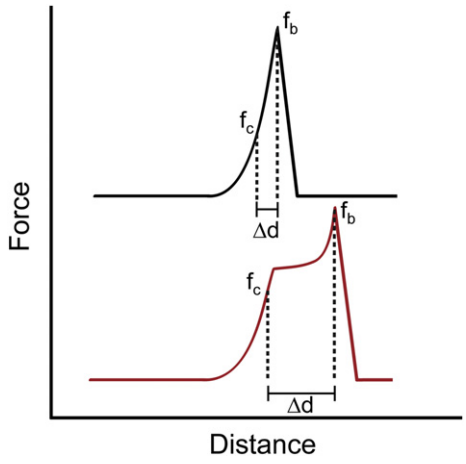

Fig. 2. Once conformational entropy is exhausted covalent bonds begin to deform (f_c), resulting in bond scission (f_b) over a narrow strain window (Δd) (top). Molecular stress relief increases the "active strain window" (bottom).

The final design principle for our initial efforts is that the activated mechanophores are able to form new bonds within the material in its load-bearing environment. Mechanochemically induced cross-linking could in principle serve either to prevent a loss in mechanical properties [13] under what is typically a destructive load, or to restore them during periods of relaxation between periodic stress events. In order to lead to improved properties, the number of constructive bond-forming events must also be effective on the macroscopic level. That is, they should create not only new bonds but also stress-bearing sub-chains akin to those lost or threatened due to the mechanical damage. These considerations tie to the two previous design criteria, because (a) multiple mechanophores per chain provide a mechanism for having multiple bond-forming events accompany each bond-breaking event (although we acknowledge that triggering catalytic systems [34,35,62,63] also holds promise in this regard), and (b) because it seems that forming a bond to a highly stressed chain prior to scission is unlikely to redistribute the force, as the formed bond must have some "slack", else it would be unlikely to form. In this framework, creating additional slack in the highly stressed bond might prove quite useful.

Depending on the nature of the applied load, the stresses experienced by the material may be highly localized, and mechanically active domains might need to be present in high concentration along the polymer backbone in order for an appreciable amount of chemical remodeling of the network to occur. There are obviously many layers of questions regarding these three design criteria (which, despite the arguments that motivate our approach, we acknowledge are not certain to be either necessary or sufficient). This includes fundamental questions about molecular stress distribution, the necessary density of mechanophores, the necessary extent of molecular stress relief, and the dynamics and time scale of all processes. When taken together, the successful realization of these criteria represents a potential pathway to stress-responsive, molecular scale properties that might permit what amounts to "mechanochemical annealing" -molecular responses that redistribute an applied stress to maximize the ultimate strength of a polymer or polymer composite (Fig. 3).

1.3. gem-Dihalocyclopropane functionalized polymers

The vision of reactions that occur along a polymer backbone under tension while leading to an increase in polymer contour length and mitigating molecular weight degradation is best satisfied by mechanophores that undergo ring opening reactions, since the reaction can occur without the polymer chain breaking. While early examples of mechanophores included those that undergo force-induced electrocyclic ring opening reactions [29,32], the macroscopic consequences (if any) of creating mechanophore-rich polymers were unknown. Wanting to probe this idea, we looked initially to *gem*-dihalocyclopropane (*g*DHC) moieties because of their simple synthesis [64] and known ability to participate in thermally accelerated electrocyclic ring opening reactions to generate 2,3-dihaloalkenes [65–68] (Fig. 4). In consideration of our first design criterion, the accessibility of these units enables their plentiful incorporation along the backbone of most alkene-containing polymers. *g*DHC-bearing polybutadiene was first reported by Pinazzi et al. in 1965 [69], and has been studied for decades [70–73] in part because of its potential as a flame retardant [74]. In addition, if the thermal rearrangement could be triggered mechanically, the *g*DHCs would satisfy our second and third mechanophore requirements: the product 2,3-dihaloalkene is longer than the parent *g*DHC, and it also possesses an allylic halide that, especially for the bromide, is susceptible to nucleophilic substitution reactions to which the *g*DHCs are relatively inert (Fig. 4). Additionally, by varying the halogen atoms in *g*DHC polymers, a rich array of reactivities, intermediates, and products can be accessed, a trait that can be exploited to gain insight into fundamental aspects of force-induced reactivity.

The history of our work on these systems provides an outline for the remainder of this article, with each of the *g*DHCs playing its own unique role, from demonstrating that *g*DCCs undergo mechanically assisted ring opening reactions, to quantifying the ring opening of *gem*-dibromocyclopropanes (*g*DBCs) using single-molecule force spectroscopy (SMFS), showing evidence of solid state activation, extending the lifetime of and subsequently trapping a *gem*-difluorocyclopropane (*g*DFC) isomerization transition state, and discovering the existence of one of the few known "mechanical only" reactions. In the remainder of this review, we will elaborate on these studies and their relationship to each other. We offer an in depth critique of how these results impact, reinforce, and challenge our current views on force-coupled chemical reactivity in polymers. We then extend these implications to broader topics in polymer and material science. As described in the following sections, these mechanophores have proven to be versatile, allowing us to probe mechanical activity in single molecules, sheared polymer solutions, and the solid state. They have provided insights into molecular stress distributions, the nature of chemomechanical coupling in polymers, and the mechanism and dynamics of mechanochemical reactions, and they have provided proof-of-concept examples of multi-mechanophore response, molecular stress relief, and mechanochemical strengthening under destructive load.

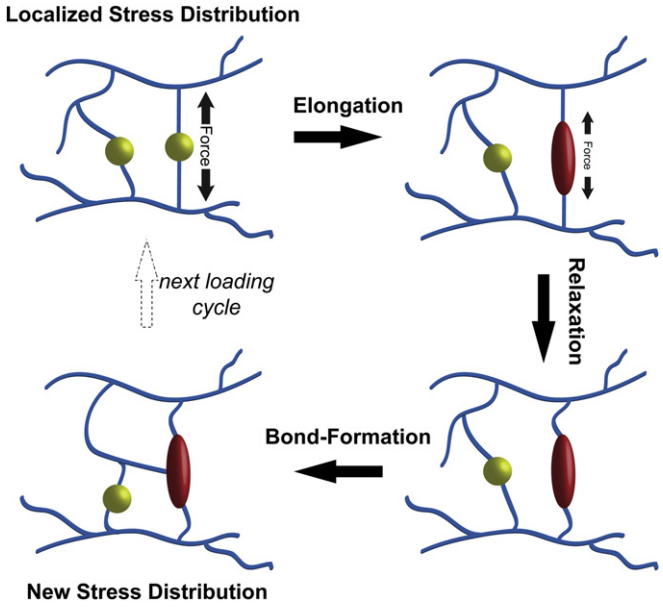

Fig. 3. Schematic of the mechanophore strategy. Under stress, mechanophore activation leads to local elongation. Subsequent relaxation (either local or global) allows for new covalent bond formation. High mechanophore content then allows for stress response at the remodeled site or elsewhere in the material.

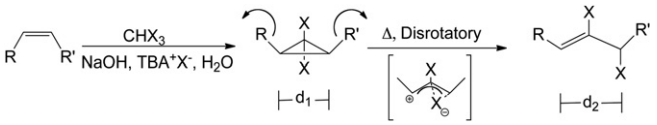

Fig. 4. Synthesis and thermal activation of dihalocyclopropanes to 2,3-dihaloalkenes.

2. Mechanochemical activity of poly(*g*DHCs)

2.1. Demonstrating mechanical activity

At the outset of our exploration into these compounds we questioned: (1) whether or not the thermal reaction (Fig. 4) could be triggered mechanically, and, if so, (2) whether large numbers of *g*DHCs could be activated under conditions that led to a single chain scission event. To answer these questions, we first employed the sonochemistry of polymer solutions. Polymer sonochemistry has a long tradition, dating back to studies by Schmid on the effect of sonication on the viscosity of polymer solutions in the 1930s [75]. In recent years, this method was re-popularized by Sijbesma as a method for screening a richer range of mechanical responses in polymers [23]. When solutions are exposed to ultrasound, oscillations from high to low pressure cause the formation of cavitation bubbles that, upon collapse, generate a radial shear field. Polymer chains that reside sufficiently near the collapsing bubble wall experience a velocity gradient along the chain that can cause various levels of uncoiling, bond deformation, and scission. This fundamental mechanism has some ramifications for the response of polymers to ultrasonic shear. First, bond scission occurs more readily in polymers of higher molecular weight [76,77] and this scission is more probable at the midchain [78,79]. These factors come into play for the poly(*g*DHC)s when discussing activation domains and ring opening efficiency. Second, environmental factors affect the sonication efficiency and the forces reached during cavitation events. In this category, it can be said that bond scission occurs more readily at low temperatures, in low vapor pressure solvents, at higher ultrasound intensity, and at lower polymer concentrations [77,80]. In some instances, additional solvation effects occur in solvents that encourage more stretched conformations, reducing the burden for mechanical work to overcome some of the conformational entropy and encourage a coil-stretched transition [81]. We also recognize an empirical value referred to as "limiting molecular weight" that we define as the lower limit of molecular weight (typically ~40 kDa, although varying with conditions and the nature of the polymer) necessary to obtain shear forces that are significant enough to cause

mechanochemical activation and chain scission, an effect that is particularly important in discerning between possible thermal and mechanical processes during sonication.

Sonication therefore provides a general method for screening the activity of mechanophores that are coupled to the main chain of polymers, and it was the basis for our first investigations into the covalent mechanochemistry of *g*DHCs. Whereas sonochemistry is a robust method to effect mechanochemical transformations and qualitatively establish their viability, at present it has limited utility as a quantitative link to potential material applications and/or the determination of kinetic and thermodynamic parameters of mechanochemical events. Furthermore, because the applied shear forces are transient, sonication must be used thoughtfully when promoting changes that are reversible on the time scale of the experiment.

The synthesis of the *g*DHC polymers is straightforward, as the functionalization of polybutadiene and natural rubbers by dichlorocarbene has been known since the 1960s [72,73]. While it seems almost certain that these polymers were sonicated at some point during the early decades of their use, the force-induced ring opening reaction remained unrecorded until 2009, when we first reported the mechanochemical activation of *g*DHC functionalized polymers under ultrasonic shear flow in solution [82]. Commercial polybutadiene was subjected to *gem*-dichlorocyclopropanation under aqueous phase transfer conditions using known procedures, resulting in polymers in which 5–72% of the alkenes were cyclopropanated. When subjected to ultrasound-generated elongational shear, we observed that *g*DCCs along the backbone underwent an electrocyclic ring opening to form the desired 2,3-dichloroalkenes in high quantity by ^{1}H NMR, with the ability to exceed 80% ring opening (based on initial *g*DCC content) at sufficient sonication times (Fig. 5).

Because bubble collapse is known to generate enormous, localized temperature increases [83], the potential role of thermal activation in sonochemical processes is often questioned. It is relatively straightforward, however, to rule out thermal effects through appropriate control experiments. In our system, for example, one telling control is the sonication of dichlorocyclopropanated polybutadiene (poly(*g*DCC)) with a high *1,2*-butadiene content. The *g*DCCs thus formed are not coupled to the polymer backbone, and therefore are also decoupled from the shear-induced tensile forces. No ring opening reaction of the side-chain mechanophores was observed under conditions in which main chain mechanophores are highly activated, ruling out thermal contributions and supporting the mechanochemical nature of the reaction. In addition, when poly(*g*DCC) of molecular weight well below the "limiting molecular weight" was sonicated, no ring opening was observed. Again, thermal effects should be effectively the same for the lower molecular weight system, further supporting a mechanochemical mechanism for activation.

We observed that approximately 35% of the *g*DCCs underwent ring opening by the time the average polymer chain had undergone one scission event, a result that held for several polymers of varying molecular weight and *g*DCC content. The magnitude of the response was especially encouraging, in that it demonstrated that the *g*DCC ring openings are triggered much more easily than destructive chain scission reactions. This activity corresponds to the generation of hundreds of reactive moieties per single chain fracture, demonstrating that the platform might be useful as a highly efficient network-forming, stress-responsive system.

Mechanistic insight was provided by comparing the relative reactivity of *cis* and *trans* *g*DCC isomers. Previously reported data show that small molecule *cis*-*g*DCC reacts 20 times faster than the *trans* isomer under thermal conditions [84]. Under sonochemical conditions, however, the extent of *cis* ring opening is only 1.35 times greater than the *trans*. Because the mechanical force is applied in a disrotatory fashion to the *cis* isomer but a conrotatory fashion to the *trans* isomer, it is expected that the thermal disrotatory reaction would be accelerated more at a given force for the *cis* isomer than the *trans*. In other words, the mechanochemical reaction should be even more selective for the *cis* isomer, not less. We therefore attributed the muted selectivity to the presence of very high forces that create large, localized regions of high stress in which virtually all *g*DCCs activate; that is, both reactions are accelerated to the point that they are quantitative, so that any additional acceleration in the *cis* does not matter. The size of the activation zone is larger for the *cis* isomer, due presumably to its greater inherent reactivity and better coupling between the direction of the applied force and the motion of the force-free reaction.

This model is supported by previous computational studies by Martínez and coworkers [85] showing non-degenerate force coupling along mechanistically different ring opening pathways. The large forces implicated, and presence of zones in which "everything reacts", further enforces the difficulty in programming selectivity into ultrasound based mechanochemistry [24,26,27,34]. This lack of selectivity is not, as we discuss in the next section,

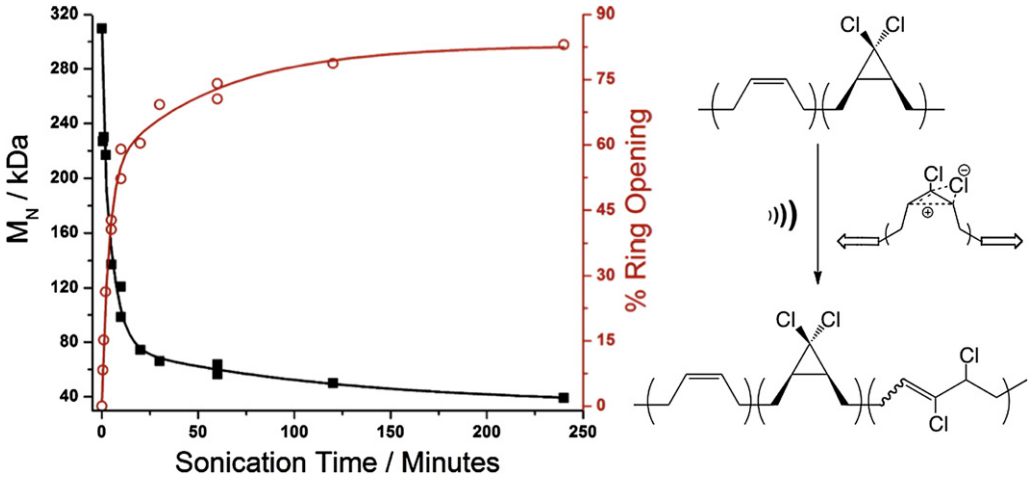

Fig. 5. Right: Sonochemical activation of *gDCC* polymer leads to the formation of 2,3-dihaloalkenes. Left: Percent ring opening and molecular weight plotted vs. sonication time. Adapted with permission from Lenhardt, J. M., Black, A. L., & Craig, S. L. gem-Dichlorocyclopropanes as Abundant and Efficient Mechanophores in Polybutadiene Copolymers under Mechanical Stress. *Journal of the American Chemical Society, 131*(31), 10818–10819. Copyright (2009) American Chemical Society.

characteristic of mechanochemistry in general, but rather is fairly specific to the exceptionally high shear forces generated during ultrasonication.

2.2. Quantifying mechanochemical activity

The sonochemical experiments were quite useful in verifying the innate mechanical activity of the gDCCs and establishing that they are more mechanochemically active than chain scission processes. The experiments did not, however, provide quantitative information regarding the force-vs.-rate relationships. A quantitative picture required a different method whereby we could apply known forces in a controlled manner, while simultaneously observing the induced reactivity in the mechanophores.

We therefore turned to single-molecule force spectroscopy (SMFS), implemented on an atomic force microscope (AFM). The experiment comprised of pulling individual *gem*-dibromocyclopropane functionalized polybutadiene (poly(gDBC)) molecules that were adsorbed to both the tip of AFM and to a silicon surface anchored to a piezoelectric stage. As the stage is pulled away from the AFM tip, the growing tension along the polymer backbone increases and is recorded by observing the resulting displacement in the AFM tip. Up to around 1 nN of tensile force, the force curves associated with these polymers are typical of those for the elastic extension of a covalent polymer, as described in Fig. 6: a low-force entropic elastic extension at low strains that gives rise to a rapid increase in force once conformational degrees of freedom have been exhausted and bond lengths and bond strengths have begun to be distorted. What is noteworthy about the gDBC polymers is that, without exception, they undergo a conformational transition at approximately 1200 pN of force that is neither predicted nor observed in conventional polymer elasticity (Fig. 6).

The observed plateau is consistent with a force-induced structural change that is coupled to an extension in the polymer contour length, as observed in conformational transitions of DNA [86], although, in contrast to the B-to-S transition in DNA, the transition in these polymers is effectively irreversible. In the case of our polymers, we attribute the transition to the ring opening of the mechanophores. The width of the force plateau is in excellent agreement with the extension expected from the quantitative ring opening of the gDBCs to the 2,3-dibromoalkene products. Importantly, the observed extension is proportional both to the pre-transition contour length and mechanophore content of the polymer. For example, a fully functionalized polymer is observed to extend by 28% of its initial contour length, the same value obtained by computational models of gDBC diads. The absolute extension corresponds to 1.28 Å per gDBC-to-2,3-dibromoalkene conversion, a value to which we return later in the discussion.

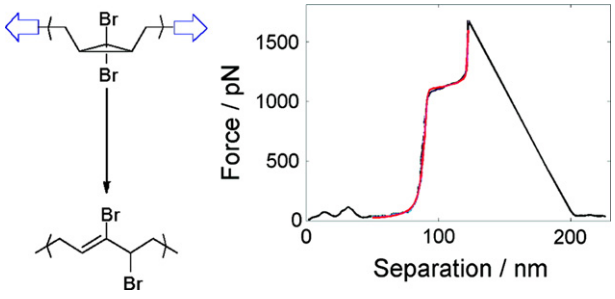

Fig. 6. SMFS of gDBC polymer results in an expanded "strain window" due to the onset of ring opening (plateau at 88 nm). Reprinted with permission from Wu, D., Lenhardt, J. M., Black, A. L., Akhremitchev, B. B., & Craig, S. L. Molecular Stress Relief through a Force-Induced Irreversible Extension in Polymer Contour Length. *Journal of the American Chemical Society, 132*(45), 15936–15938. Copyright (2010) American Chemical Society.

These observations have several implications for our objectives in materials property engineering. First, within our ability to discern it, the entire population of gDBC mechanophores is opened prior to chain detachment or chain scission. In fact, prior work by others suggests that forces of several nN are necessary to effect bond scission on the ms time scale of the SMFS experiment [61], and so the mechanophores are far more active under force than is the destructive scission event. The competition between mechanophore activity and chain scission in the ultrasound experiments is therefore attributed to the uneven force distribution along the polymers under extensional shear, a picture that is different from that generated by pure, static tension in the SMFS experiments.

Second, the observed extension potentially meets one of the challenges that we view as being critical for mechanophore-based self-strengthening polymers, in that there is a significant strain window between the onset of mechanical activity and the failure of the stress-bearing polymer sub-chain (Fig. 2). A polymer sub-chain that would typically (without ring opening) have failed at a length of 88 nm, for example, was observed to survive to 112 nm thanks to the 28% extension, demonstrating the capacity for this architecture to have a dynamic contour length that can change on the time scale of destructive load.

Third, the observed covalent chemical response leads to a new form of "force management." Lake and Thomas [87] first pointed out over 50 years ago that the energy necessary to break a load-bearing polymer chain segment is far greater than the energy of the bond being broken, because it includes the elastic energy stored among all bonds that is lost when one of the bonds finally breaks. In relationship to the SMFS experiments, this toughness of an individual polymer sub-chain, or net energy absorbed prior to rupture, is given by the total area under the force-distance curve up to the point of scission/detachment. In the case of poly(gDBC), both the magnitude of the force at the transition and the distance over which it is sustained are substantial, resulting in a toughness at the single-molecule level that is several times larger than that of a typical covalent polymer. To the best of our knowledge, the toughness observed by SMFS in the gDBC polymers is the largest demonstrated, and it is interesting to consider the consequences of such behavior for macroscopic material properties. Because the total energy absorbed by the material is spread over a large (relative to the molecular scale) volume, it seems likely that a significant effect can only result if the local "stress relief" allows nearby polymers to also reach the transition and absorb more energy. This in turn allows a third set of polymers to reach the transition and absorb more energy, and so on. Identifying the molecular design principles that create such non-linear macroscopic responses remains, to the best of our knowledge, an open challenge.

The SMFS experiments also offer an opportunity for insight into mechanochemical coupling in polymers. The validity of the chemomechanical framework for covalent reactions across length and time scales has recently been confirmed via a thorough treatment by Boulatov [40], but quantifying the effect of the coupling in various contexts (both in terms of the force transducer and the specific reaction) remains an important and ongoing challenge. For example, it is not clear whether isolated small molecule transduction, in which force of known directionality is applied directly to specific atoms, is identical to force transduction in the same mechanophores embedded within polymers. Given the large number of observable ring opening events in even a single SMFS extension curve, the gDBC platform allowed us to rapidly obtain a statistically significant number of chemical reactions and extract the desired kinetic information. The force-coupled kinetics were inferred both from the time scale over which the transition occurred at the plateau force, and through a more comprehensive treatment in which the force curve was modeled as a monomer-by-monomer

transition from one freely jointed chain to another. Both treatments yielded the same bottom line: the rate constant for ring opening at 1200 pN is approximately 10^2 s^{-1}, a factor of $\sim 10^{13}$ times greater than the extrapolated force-free value of 3×10^{-11} s^{-1} [88].

Fitting to Bell-Evans (BE) model for a Freely Jointed Chain, $k(F) = k_0 \exp(-F\Delta x^{\ddagger}/k_B T)$, led to a value of $\Delta x^{\ddagger} = 1.05 \pm 0.11$ Å, a value that does not correspond to any relevant internuclear distances determined computationally for carbon atoms at or adjacent to the *g*DBC functionality. One proposed possibility for this discrepancy is inherent to the BE model, namely the assumption that $\Delta x^{\ddagger}$ does not change based on the applied force. Alternatively, one can consider that the compliance of the system, and in particular the differential compliance of the ground state and transition state, might change as a function of force [89,90]. Force-dependent changes in the potential energy surface can be approximated by assuming a specific form of the potential energy surface, for example the cusp model. In the case of poly(*g*DBC), however, fitting the polymer extension curves assuming a cusp-like potential energy surface generated a value of $\Delta x^{\ddagger} = 1.28 \pm 0.14$ Å, still without a direct correspondence to any relevant change in internuclear distance. While "compliance" contributions might play a role, a likely contributor may be found by looking at the forces experienced by the mechanophore in the context of the directionality and transduction of forces throughout the chain. In the cases of cyclobutane ring opening, Boulatov and coworkers discovered that $\Delta x^{\ddagger}$ could be accurately interpreted as the change in internuclear distance between methylene carbons adjacent to the reactive groups [89]. This analysis benefited, however, from the fact that the projection of the force vector along the reaction coordinate could be computationally quantified [42]. In our system, the measured force is the net tension applied along the vector defined by the entire length of the polymer chain. Because not all bonds (or even necessarily any bonds) can be exactly aligned with the overall chain direction, it is difficult to establish the coupling of force to the nuclear motions that are relevant to the reaction coordinate. This idea was demonstrated computationally by Marx, who showed that the length of alkyl tethers influenced the extent of mechanochemical coupling to an embedded mechanophore [91,92]. For the case at hand, we note that the net extension of the *g*DBC polymer upon ring opening is approximately 1.28 Å, and this ultimate extension puts an upper limit on the expectation for $\Delta x^{\ddagger}$. Because the transition state of the reaction is very late, it is reasonable to expect that the effective value of $\Delta x^{\ddagger}$ would be close to, but slightly below, this value, in good agreement with the results from fitting the force curves.

2.3. Reactivity in the bulk

The end-goal of our design structure continues to be the creation of mechanically-responsive materials, specifically via the use of mechanophores that will react constructively in the bulk thus altering the macroscopic properties of the target material. While the mechanical activity of the *g*DHC system was demonstrated under ultrasonic shear in solution, and rates were quantified under tension using SMFS, it is the behavior in the bulk that is most relevant to materials science, and the relevance of the former to the latter is not obvious. For example, we saw different force distributions and active domain sizes in our systems: toward the center of the chain in sonication, and distributed throughout the entire sub-chain in AFM experiments. We wondered how forces would be distributed in the solid state.

In order to probe the reactivity of *g*DHCs in the solid state, we conducted compressions on bulk polymer samples in a steel press; the compressive force leads to large shear forces normal to the applied force. As observed in the sonochemical experiments, applied stress resulted in ring opening to the 2,3-dihaloalkenes [93]. As in solution, we were able to utilize the varying reactivities of the different *g*DHC functionalities, as well as ^{1}H NMR characterizations of microstructure in the ring opened products, to map force distributions in solid state poly(*g*DHC)s under stress. The macroscopic compression of polymer in a press led to large shear forces radiating out normal to the applied force vector, and those forces resulted in the same ring opening reactions observed in solution, but at much lower levels, typically on the order of tenths of a percent of monomer units. Greater pressures resulted in higher strain rates, and the extent of ring opening increased accordingly, although details of the specific dynamics at play are only speculative at this point.

In order to demonstrate the muted selectivity mentioned previously with the *g*DCC polymers [82], we subjected *gem*-bromochloro-cyclopropanated polybutadiene (poly(*g*BCC)) to compression and pulsed ultrasound. In both cases, the stereochemistry of the *g*DHC had an effect on the ring opening activity. The *cis-anti-g*BCC mechanophore was approximately 1.8 times more reactive than its *cis-syn-g*BCC isomer. This is analogous to the sonochemical case and in contrast to the thermally obtained Woodward–Hoffman [94–97] allowed selectivity of 970:1 in previously reported solvolytic conditions [68]. We were able to observe and distinguish ring opened diads from isolated ring opened products by ^{1}H NMR, allowing for some determination of mechanically active domains in the solid state. The average length of these domains was on the order of 4 monomers. Given the small amount of opening overall, this is a higher degree of correlation than would be expected in a random thermal opening, but shorter than the entanglement spacing expected in a polymeric network [98].

These results may be explained through several different effects, for example that entanglement spacings are polydisperse and the result may reflect that smaller spacings are more highly stressed than their larger counterparts. Second, it is possible that local stress relief occurs on the time scale of the deformation, reducing the load on other monomers within the entanglement region. Third, the forces may differ greatly due to topological structure, proximity to the direct entanglement point, knotting, etc…, all of which are difficult to analyze by conventional methods. Regardless of the origin, the presence of a high mechanophore density appears to be necessary in order to guarantee activation in regions of high stress; if only 1 out of 5 repeat units contained a mechanophore, there would be regions of high stress but perhaps no mechanochemical response.

2.4. Diblock copolymers "in a snap"

Encouraged by our ability to direct ring opening to specific domains along the polymer backbone, we returned to solution based sonochemistry in order to probe the domain effects where the degree of activation was large and presumably localized. In the ultrasonic degradation of poly(*g*DCC) to an average of one scission per chain, for example, we anticipated that on average the two resulting chains would possess AB diblock character, with an unactivated *g*DCC rich (A) block, and a 2,3-dichloroalkene rich (B) block (Fig. 7A). The relative sizes and purity of the blocks would provide information as to the force distributions across the polymer chain during the course of the scission event. The blocky character of activated regions was supported first by ^{1}H NMR analysis, where the chemical shifts of the 2,3-dichloroalkene varied depending on whether the product was adjacent to a *g*DCC or another 2,3-dichloroalkene. Second, we set out to chemically separate the blocks. This was accomplished by ozonolysis of the alkene products, allowing for the intact non-activated *g*DCC segments to be isolated (Fig. 7B). The molecular weight of the *g*DCC blocks following ozonolysis matched the average *g*DCC content of a post-sonicated polymer chain, indicating that the *g*DCC blocks were effectively "pristine" within the limits of detection.

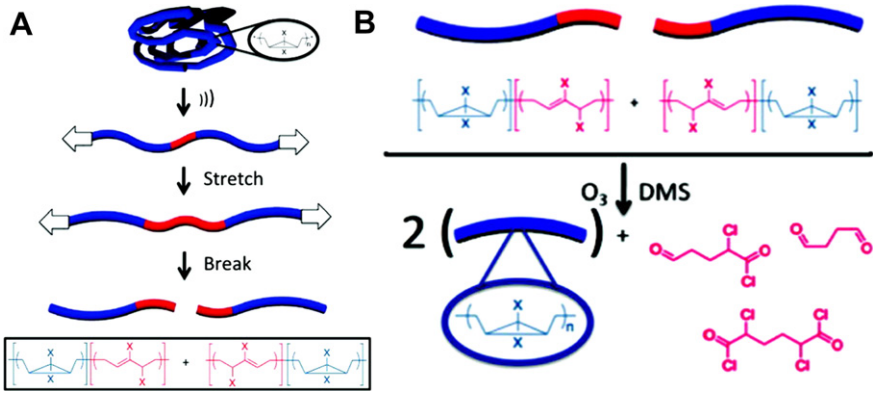

Fig. 7. A: Pulsed ultrasound of *g*DCC results in diblock copolymers. B: Ozonolysis of diblocks allows for the isolation of pure *g*DCC fragments. Adapted with permission from Black Ramirez, A. L., Ogle, J. W., Schmitt, A. L., Lenhardt, J. M., Cashion, M. P., Mahanthappa, M. K. et al. Microstructure of Copolymers Formed by the Reagentless, Mechanochemical Remodeling of Homopolymers via Pulsed Ultrasound. *ACS Macro Letters*, 23–27. Copyright (2011) American Chemical Society.

Given the range of distinct phase behavior known to exist in diblock copolymers, the bulk properties of the sonicated polymers were characterized by differential scanning calorimetry (DSC) and small-angle X-ray scattering (SAXS). DSC analysis of a 134 kDa *g*DCC polymer sonicated to 67 kDa showed the presence of two glass-transition temperatures (T_g), which suggested the possibility of micro-phase separation into chemically distinct domains. This suggestion was confirmed by SAXS, which was performed above and below the T_m of the semicrystalline poly(*g*DCC) and showed well defined lamellar spacing of 27 nm (Fig. 8).

This method of block copolymer synthesis (almost literally "in a snap") has interesting potential in the fields of polymer synthesis and material science. The formation of diblock copolymers via pulsed ultrasound can be viewed as an extreme example of regio-selectivity. The many cyclopropanes along the polymer backbone have identical intrinsic reactivity, but only those located near the middle of the chain at the instant of chain rupture have been converted to 2,3-dihaloalkenes. This leads to the formation of discrete blocks, but it also serves as the basis for "on demand" activation in regions of high stress within macroscopic materials.

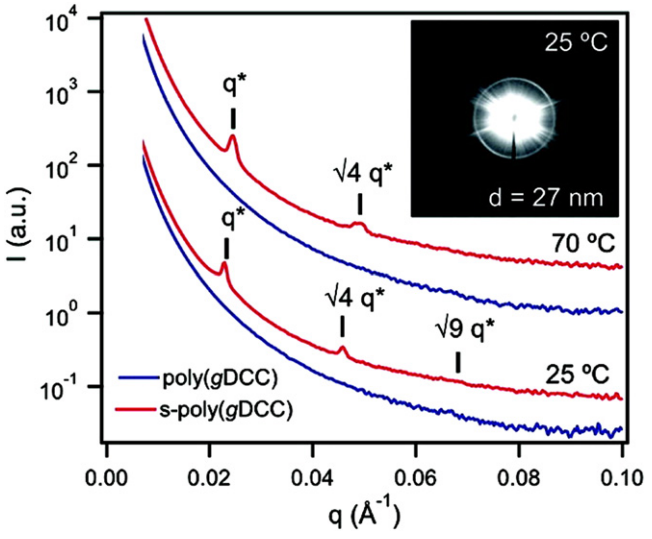

Fig. 8. SAXS of sonicated poly(*g*DCC) shows long range order both above and below the T_m of the sample. Reprinted with permission from Black Ramirez, A. L., Ogle, J. W., Schmitt, A. L., Lenhardt, J. M., Cashion, M. P., Mahanthappa, M. K. et al. Microstructure of Copolymers Formed by the Reagentless, Mechanochemical Remodeling of Homopolymers via Pulsed Ultrasound. *ACS Macro Letters*, 23–27. Copyright (2011) American Chemical Society.

2.5. High exchange substitutions in the bulk

As mentioned in the introduction, one of our long-term goals is to trigger constructive bond-forming chemistry in the solid state. An open question, however, was whether the activation of an intramolecular reaction could be coupled to a subsequent intermolecular reaction in the bulk. Given that the generation of 2,3-dihaloalkenes occurred in the bulk and at room temperature, we targeted nucleophilic substitution of the allylic halide as a viable bond-forming reaction. The concept was tested and established by extrusion, resulting in levels of ring opening of between 2 and 32% depending on the halogens, extrusion rate, time, and temperature.

More importantly, however, was the observation of *in-situ* nucleophilic substitution reactions occurring during the solid state extrusion process (Fig. 9). When a *g*DBC polymer was extruded in the presence of benzyl triethylammonium chloride for 20 min at 60 °C and 100 rpm, subsequent ^{1}H NMR analysis established that substitution of the allylic bromide by chloride ion occurred in over half of the ring opened products. When molecular weight was analyzed, this corresponded to an average of over 500 ring openings and 250 substitution reactions for every 9 scission events per polymer chain (initial polymer: 67% *g*DCC, 490 kDa). This corresponds to over 25 new intermolecular covalent bond formations per covalent bond scission, and it represents what we believe to be the first example of tandem mechanochemical activation and substitution reaction in the bulk. This result provides a strong indication that it is possible to leverage stress-induced reactivity to trigger cross-linking chemistry in the solid state, a concept that has the potential to preserve or improve the integrity of a polymer network under destructive mechanical loads.

3. Tension trapping and new reactivity

3.1. gem-Difluorocyclopropanes

While a primary goal of polymer mechanochemistry is to enhance bulk material properties, there also exists the potential to create new chemistry that proceeds along pathways that are

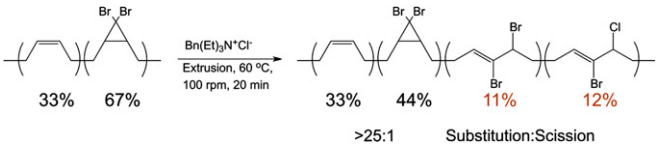

Fig. 9. Extrusion of poly(gDBC) in the presence of a nucleophile results in high efficiency nucleophilic substitution in the solid state.

inaccessible in force-free regimes. As previously mentioned, this has been elegantly demonstrated by others in the Woodward–Hoffmann disallowed ring opening of BCB [28], and the mechanical reconfiguration of atropisomers [33]. Fundamentally, this is based on the directionality of applied force, however we have recently demonstrated that reactions can be created that leverage the highly localized nature of this applied force.

In contrast to other *g*DHCs, which undergo electrocyclic ring opening reactions to form 2,3-dihaloalkenes, the *g*DFC moiety is known to undergo a thermal isomerization via a 1,3-diradical transition state [99]. This isomerization is observed when a poly(*g*DFC) is synthesized with a *cis* to *trans* ratio of 1:1.2. Subsequent thermal equilibration overnight at 210 °C gives a *cis* to *trans* ratio of 1:2.6, consistent with the ~1 kcal/mol stability difference between isomers. As with the ring opening reactions, the isomerization can be accelerated dramatically by mechanical force, nearing completion in less than an hour at ~5 °C when subjected to pulsed ultrasound. Surprisingly, however, the direction of the reaction is reversed. Sonochemical isomerization gives a *cis*:*trans* ratio of 3.5:1. Notably, the ultimate *cis*:*trans* ratio is limited largely by the size of the mechanically active zone, and 95–98% of activated *trans* isomers end up as *cis* cyclopropanes [100].

The result is qualitatively intriguing on two fronts. First, the mechanical isomerization leads to the less stable isomer, and so the covalent polymer structure can be reversibly switched between predominantly *cis* vs. *trans* states in response to ultrasound and heat, respectively. This behavior constitutes a reversible "mechanoswitch", reminiscent of azobenzene and other photoswitches. Second, the mechanically generated *cis*-*g*DFC has a shorter end-to-end distance than does the *trans*-*g*DFC, leading to the counterintuitive result that the mechanophore undergoes a net contraction in response to being pulled [100] (Fig. 10).

This behavior is rooted in the formation and "tension trapping" of the *s*-*trans*/*s*-*trans* diradical transition state as a global minimum on the force-coupled potential energy surface under the transient shear-induced tension. The diradical persists until the tension relaxes, either at the end of the bubble collapse or in response to chain scission, at which point the diradical undergoes an orbital-symmetry preferred disrotatory ring closing to the *cis*-*g*DFC. Extensive *ab initio* molecular dynamics simulations were performed to determine the force regimes and time scales over which these transformations occur. The application of 2 nN of force to *cis* attachments resulted in 6 out of 20 *g*DFCs opening in the disrotatory (allowed) pathway within 1 ps, whereas the remaining 14 did not open (though would be expected to over a longer time scale). The application of 3 nN was required to observe ring opening for the *trans* attachments, giving a result of 1 conrotatory (disallowed) opening out of 20 trajectories within 1 ps. Moreover, ring closure is not observed on the ps time scale, reinforcing the hypothesis that this occurs upon stress-free chain relaxation. Upon relaxation, the force-free ring closure is calculated to occur within 500 fs and proceeding through the thermally allowed (disrotatory) pathway in 95% of cases. A net contraction in contour length of ~7% per monomer occurs with each *trans* to *cis* isomerization event, in stark contrast (and perhaps complement) to *g*DCCs and *g*DBCs, for which contour length increases with each ring opening event. This counterintuitive result demonstrated the first evidence that the *g*DFC system was capable of undergoing mechanical only reactions, in this case the selective formation of the isomer that is neither kinetically nor thermodynamically favorable under force-free conditions.

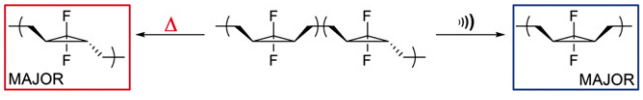

Fig. 10. Thermal (*trans*) vs. sonochemical isomerization (*cis*) for poly(*g*DFC). From [100]. Reprinted with permission from AAAS.

The *ab initio* simulations indicated that the 1,3-diradical that results from *g*DFC ring opening becomes a local minimum on the force-modified potential energy surface at forces greater than 1 nN, and a global minimum above 3 nN (Fig. 11). This near-inversion of the potential energy surface suggested that the 1,3-diradical may be stabilized sufficiently to participate in bimolecular addition chemistry. Gratifyingly, sonication of the *g*DFC polymer in the presence of coumarin-2,2,6,6-tetramethylpiperidine-1-oxyl (CT) adduct resulted in CT addition to the *g*DFC radical, a reaction that cannot occur on the force-free potential energy surface (Fig. 12). The rate constant for nitroxide addition is likely on the order of, or less than, 10^8 M^{-1} s^{-1} [101], and so the observed trapping efficiency of 1–2% corresponds to a diradical lifetime on the order of 10^{-9} s or longer.

Further work has recently shown that multiple diradicals can be trapped in proximity to one another, allowing a new radical elimination reaction to take place between them. The key observation is that the extent of isomerization relative to chain scission varied with the net *g*DFC content of the polymer; higher *g*DFC content gives lower levels of isomerizaton [102] (Fig. 13). This behavior differs dramatically from that of the *g*DCCs and *g*DBCs, for both of which isomerization is independent of *g*DHC content, and it suggested that adjacent *g*DFCs might behave differently than *g*DFCs that are isolated between nascent butadiene monomers.

The microstructure hypothesis was tested by synthesizing via ring opening metathesis polymerization (ROMP) a polymer of 33% *g*DFC content in which a *g*DFC was on every third repeat unit, so that no adjacent *g*DFCs were present. The isolated *g*DFC polymer is a clear outlier from the trend established as a function of *g*DFC content with randomly functionalized polymers, as it exhibits a higher percent isomerization per scission cycle than even the lowest random content polymer tested (5% *g*DFC) (Fig. 13). In contrast, when large numbers of adjacent *g*DFCs were introduced directly through synthesis, the extent of isomerization dropped to an extent that is consistent with a quantitative relationship established on the basis of the adjacent *g*DFC content of random copolymers. These experiments confirmed that polymer microstructure, and not simply the total *g*DFC content, is responsible for the observed reactivity trends.

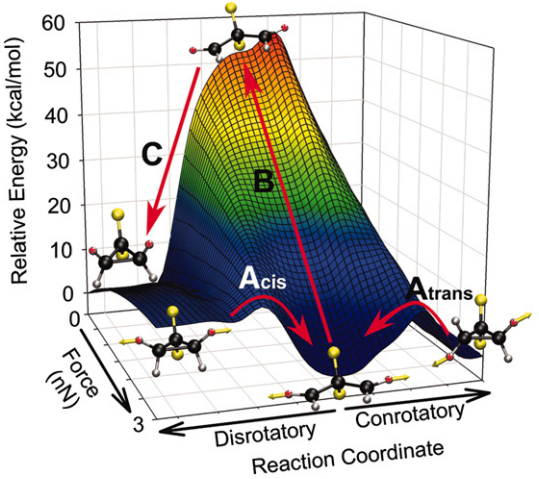

Fig. 11. At high force, diradical transition state becomes a global minimum on the potential energy surface (A). Upon relaxation (B) ring closure occurs along the thermally allowed disrotatory pathway (C), resulting in the *cis* isomer. From [100]. Reprinted with permission from AAAS.

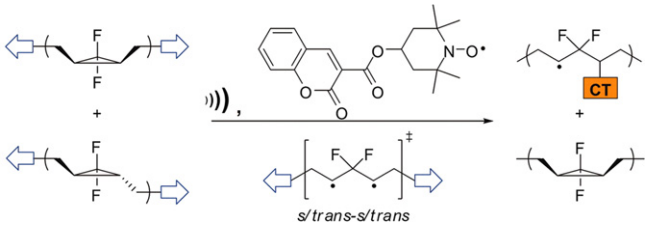

Fig. 12. Sonication of poly(*g*DFC) in the presence of CT trap results in trapping of the diradical transition state. From [100]. Reprinted with permission from AAAS.

The requirement for adjacent *g*DFCs and the detection of 3,3-difluoroalkene end group products by ^{1}H and ^{19}F NMR led us to propose a mechanism whereby adjacent 1,3-diradicals disproportionate via elimination of the central 1,4-diradical (Fig. 14a). The scissile bond is weaker than a conventional covalent bond, and so chain scission occurs earlier in the stretching of the polymer chain, resulting in a lower extent of *g*DFC opening/closing and isomerizaton (Fig. 14b). The mechanism is consistent with the experimental observations, intuitively satisfying, and, importantly, confirmed by *ab initio* simulations, which at 3 nN of simulated force showed the rapid formation of adjacent diradicals followed by the proposed disproportionation. The force-induced reactivity is somewhat remarkable, because the force-free transition state of this elimination (really a "transition state upon transition states") would correspond to an activation energy in excess of 120 kcal mol^{-1}, pointing further to the remarkable potential of mechanical force to create reaction pathways that are impossible by other means and presenting a framework for creating "mechanical only" response in materials.

The PB-co-*g*DFC polymer represents a versatile system that can potentially partake in a rich array of chemistry and be synthesized from relatively inexpensive commercially available components in one step. As with the *g*DBCs studied by AFM, the contour length modulation is particularly intriguing, although here it is a contractile, rather than extensile, response. If a force regime can be reached where isomerization occurs and chain scission is eliminated, we can imagine the chain length contracting under a mechanical load and re-extending under subsequent thermodynamic equilibration (*cis* to *trans* thermal annealing). Furthermore, the mechanically generated radicals in this system are truly unique relative to force-free chemistry. The 1,3-diradical has been shown to exist long enough to participate in radical trapping, and we believe this or similar non-scissile radical generation could be leveraged to induce interchain cross-linking under mechanical stress. From a mechanistic perspective, the disproportionation reaction is also unique relative to the molecular process, given that the steady-state concentration of diradicals is effectively zero under force-free conditions. In a broader sense, this demonstration of tension trapping an extremely transient species suggests a possible route to the spectroscopic observation of these and similarly elusive and exotic species and electronic states.

3.2. Thermally remendable perfluorinated mechanophores

These studies on the *g*DFC system led us to further explore the mechanochemical potential of polymers bearing polycyclic fluorinated backbones. For all of the *g*DHC polymers studied, the chain scission process is irreversible. The engineered mechanochemical outcomes produce ring opened products, but molecular weight degradation is still predominantly caused by carbon–carbon bond scission. Looking to add a reversible scission "failsafe" onto the

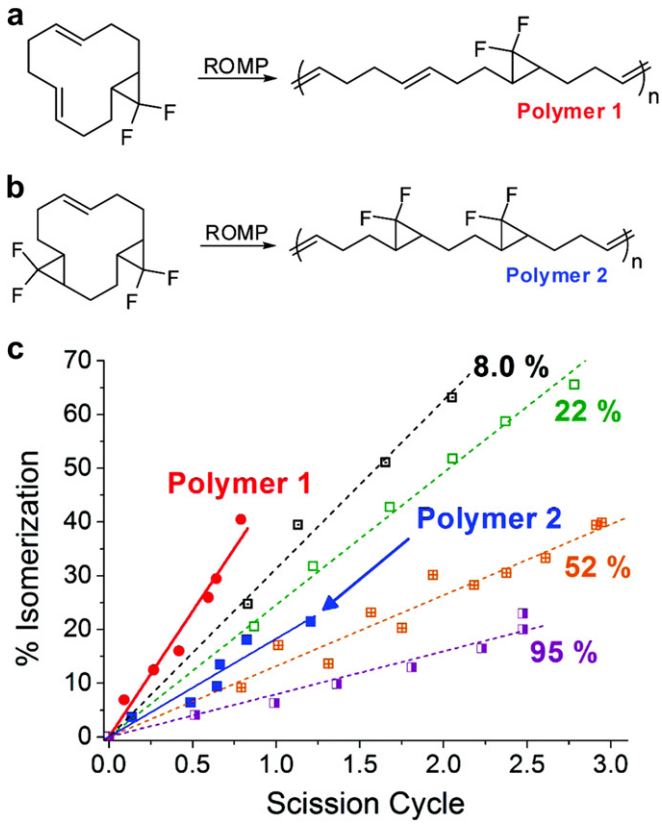

Fig. 13. Percent isomerization vs. scission cycle decreases with increased *g*DFC incorporation. Polymers 1 and 2 are outliers from this trend. Reprinted with permission from Lenhardt, J. M., Ogle, J. W., Ong, M. T., Choe, R., Martinez, T. J., & Craig, S. L. Reactive Cross-Talk between Adjacent Tension-Trapped Transition States. *Journal of the American Chemical Society, 133*(10), 3222–3225. Copyright (2011) American Chemical Society.

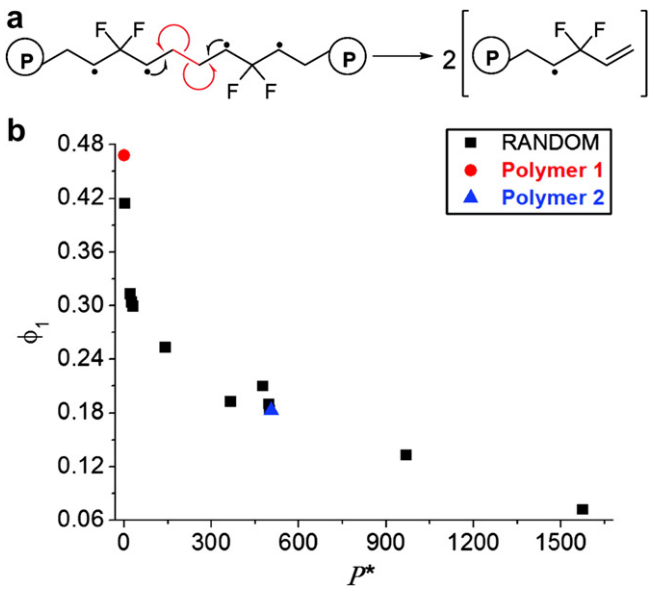

Fig. 14. a: Adjacent diradical intermediates allow for disproportionation and premature chain scission. b: Percent isomerization per scission cycle (Φ_1) correlates with the probability of adjacent *g*DFCs. Reprinted with permission from Lenhardt, J. M., Ogle, J. W., Ong, M. T., Choe, R., Martinez, T. J., & Craig, S. L. Reactive Cross-Talk between Adjacent Tension-Trapped Transition States. *Journal of the American Chemical Society, 133*(10), 3222–3225. Copyright (2011) American Chemical Society.

main chain, we were influenced by the work of first Wudl [37], and later Bielawski [36], that showed the mechanochemically induced retro-Diels-Alder reactions along polymer backbones. We were further encouraged by the work of Sijbesma, showing the indefinite restoration of molecular weight after the mechanochemical rupture of coordination bonds [23,24,34]. To fulfill the requirement of high content and coupling to tension along the polymer backbone, we looked to a family of perfluorocyclobutane polymers (pPFCBs) [103]. The synthesis of these polymers is known to proceed through the step-growth dimerization of aryl bis-trifluorovinyl ethers (TFVEs) via a diradical intermediate at elevated temperatures (150–200 °C), but thermal degradation occurs primarily to hexafluorocyclobutene and phenol products. We sought to establish that under stress we could bias the degradation to the TFVE end groups which could subsequently be repolymerized (Fig. 15) [103]. Previously, the generation of TFVE end groups was observed by infrared spectroscopy (IR) during crack formation in cross-linked pPFCB networks [104]. Alternate mechanisms and competing pathways were not characterized in the solid state work, and we set out to characterize the mechanochemistry of PFCBs.

When we subjected our pPFCB polymer to standard sonochemical conditions, we were able to achieve a drop in molecular weight from 115 kDa to 10 kDa, with the only detectable changes in structure being the conversion of PFCB groups to TFVE groups, as confirmed by both ^{1}H and ^{19}F NMR. Relative integrations of these transformations corresponded with the expected drop in molecular weight determined by size-exclusion chromatography with multi-angle laser light scattering (SEC-MALLS). Small scale thermal remending was then performed on the sonicated polymer, with an increase in molecular weight from 10 to 37 kDa and corresponding loss in TFVE end group, as characterized by ^{19}F NMR. Given that there is a rich array of available pPFCBs, we sought to demonstrate that this effect was not unique to the biphenyl-ether based polymer (Fig. 15), and similar results were observed for a bis-aryl hexafluoroisopropylidene based PFCB ether polymer.

We hypothesized that the mechanochemical conversion of PFCB to TFVE proceeds through a 1,4-diradical intermediate, the microscopic reverse of the step-growth polymerization. Mechanistic studies supported this hypothesis. Analysis by ^{19}F NMR provided us with insight into and further proof of the proposed diradical mechanism. The thermal polymerization produces a stereorandom

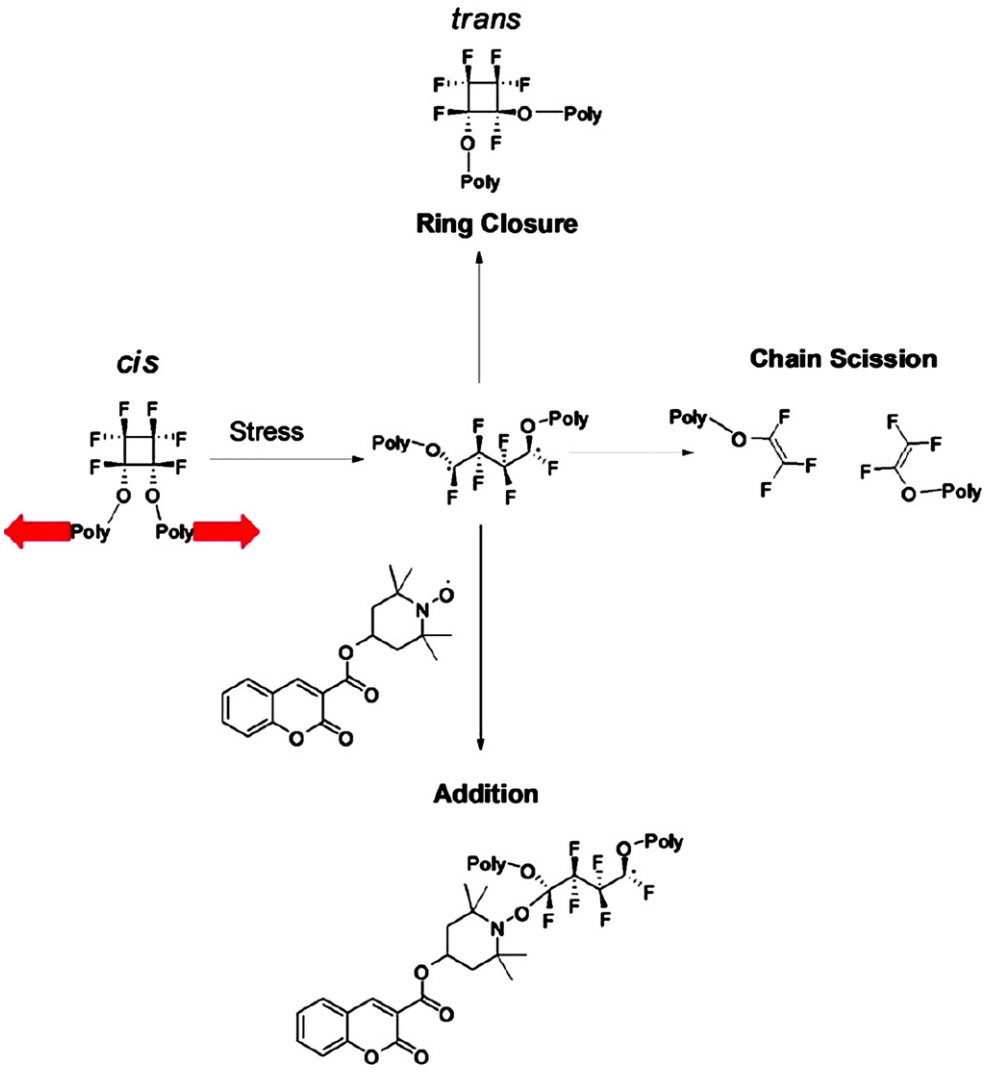

Fig. 15. Sonochemical ring opening of cis isomer (disrotatory) can result in chain scission, isomerization to the trans isomer, or labeling in the presence of the CT trap. Reprinted with permission from Klukovich, H. M., Kean, Z. S., Iacono, S. T., & Craig, S. L. Mechanically Induced Scission and Subsequent Thermal Remending of Perfluorocyclobutane Polymers. *Journal of the American Chemical Society, 133*(44), 17882–17888. Copyright (2011) American Chemical Society.

polymer (i.e. the initial polymer sample) with a *cis*:*trans* ratio of 48:52. We observed an increase in the overall *trans* content with increased sonication time, establishing that the C3–C4 bond in many PFCBs must break without complete scission of the PFCBs to TFVEs. The isomerization might result either from preferential ring opening of the *cis* isomers or preferential ring closure to the *trans* (or both), but in either case it offers an additional example of backbone remodeling in response to mechanical force. As in previous experiments, the polymer was sonicated in the presence of the CT radical trap, and CT incorporation was observed and quantified by SEC-UV–Vis. It is worth noting that the PFCB isomerization and associated tension trapping of main chain radicals occurs here within a family of well-known commercial polymers, offering some hope that the concept of mechanochemical remodeling might be applicable outside of the academic laboratory.

4. Challenges and future directions

The success of our proposed approach to the construction of stress-responsive/self-healing materials relies on: our ability to construct polymers that (1) have high mechanophore content, (2) increase in contour length when stressed, and (3) generate the ability to participate in bond-forming reactions. In the past several years, this trajectory has proven fruitful, as we have developed working model systems that meet all of these criteria. In this regard, the demonstration of mechanical activity in *g*DHCs has proven to be quite enabling, given the ease of synthesis and high degrees of functionality attainable. With this system, we have demonstrated dramatic increases in single-molecule contour lengths under stress (and corresponding increases in toughness at the single-molecule level), and extents of backbone remodeling that would have not been possible in polymers containing only one mechanophore. Several results have been deviations from our path of rational design. The *g*DFC system proved rather propitious in this regard, allowing us, for the first time, to trap a force-free diradical transition state as a force-coupled ground state. Complementary to this, we discovered one of the few known "mechanical only" organic transformations, where the localized nature of applied stress allows for the disproportionation of adjacent, trapped diradical transition states.

Recently, Leibler and coworkers outlined design principles for supramolecular self-healing systems. They stated that the strength of the supramolecular associations (mechanically scissile bonds) must be lower than that of covalent bonds in order to ensure availability of mending sites. It was also suggested that self-healing efficiency relies on the number of groups available to associate after fracture [105]. Given the dynamic nature of the systems we have described, we believe that purely covalent systems can fulfill the self-healing criteria set forth in the context of non-covalent networks. Traditionally, supramolecular systems with self-healing properties rely on dissociation rates that are favorable when compared to covalent bond scission and association rates that are favorable on the time scale where healing is required. As shown by us [103], Bielawski [38], and Wudl [37], covalent bonds can be designed to break in a way that they are able to reform. This can be viewed as an extreme example of Leibler's dissociative scenario. In addition, however, the *g*DHCs [82,88,93,106,107] and BCB [33] demonstrate constructive mechanochemistry, in the form of stress relief or increased reactivity, in the absence of chain rupture, allowing predominantly constructive outcomes to occur. The kinetics of ring opening (increase in contour length, and generation of functionality amenable to bond formation are also favorable with respect to homolytic bond scission. Relative to supramolecular systems, covalent networks can be completely static in a stress-free state and only undergo dissociation or activation only when stress is applied.

Moving forward, we see several hurdles to overcome as we work to better understand chemomechanical phenomena and create functional systems. The *g*DHC systems are rare examples of functional groups that can easily be embedded within a high molecular weight polymer backbone in high content. With architectural criteria for mechanical activity becoming more understood, many mechanophores with a wide range of potential transformations are sure to be demonstrated. The incorporation of a single mechanophore into a polymer chain will often be sufficient for many applications, but innovative ways to form high content materials will provide us with an additional and important challenge.

To better understand the thermodynamics and kinetics of molecules under force, it is often desirable to apply precise amounts of static tension. Controlled force is typically applied either by SMFS, as in the seminal work of Fernandez and coworkers [39,60] and our own studies [25,108], the strained macrocycles of Boulatov [41,42,89], or through the adsorption of of polymer bottlebrushes, as demonstrated by Sheiko and Matyjaszewski [109,110]. While these methods are relatively robust, high throughput remains a challenge, particularly for SMFS. For example, the ability to efficiently create orthogonal but strong chemical and physical interactions between mechanophore laden polymers and a surface and force microscope tip is often a challenge. Although much of the work involving SMFS has probed interactions in the pN force regime, the activation of covalent bonds requires attachments that can withstand forces on the order of nN, a force regime that requires much more robust attachments.

As much of our work transitions towards reactions in the bulk, and especially in network formation, analysis becomes difficult. As we begin to utilize systems that approach functional materials, it becomes more difficult to probe fundamental mechanisms just as the behavior of interest becomes increasingly complex. This is perhaps particularly true when the goal is a macroscopic response that is generated by molecular and microstructural changes, requiring probes that work across decades of length and time scales. Despite these hurdles, the ability to systematically manipulate molecular structure combined with a firm understanding of relative mechanochemical reactivity, may allow for trends in the molecular to macroscopic property relationship to be established. We are therefore actively working to apply our design principles to as broad a range of polymer systems as possible, seeking to observe the manifestation of mechanochemical response in bulk material properties such as toughness and self-healing.

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